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Determination of the kinetic data of the thermal decomposition of energetic plasticizers and binders by adiabatic self heating

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Abstract

The thermal decomposition behaviour of the following plasticizers and uncured binders (diols for PUR-type elastomer binders) was investigated in solutions of toluene (with 10 mass% contents) by adiabatic self heating with an 'accelerating rate calorimeter' (ARC$^{\text{TM}}$): uncured GAP (poly-glycidylazide) from two manufacturers, polyGLYN (poly-glycidylnitrate) mixture (58.8/41.2 in mass%) *N*-methyl-/*N*-ethyl-NENA (NENA = *N*-(2-nitratoethyl)-nitramine), DANPE (1,5-diazido-3-nitrazapentane), GAPA (short chain GAP but with azido end groups), EGBAA (ethylene glycol-bis-(α-azidoacetate), octylazide (not for use in explosives), GAP-AA-2000 (normal GAP, but OH-end groups as esters of α-azidoacetic acid), GAP-AA-500 (short chain GAP, but OH-end groups as esters of α-azidoacetic acid). Three types of energetic groups are represented with these compounds: the organic nitric acid ester group, the nitramine group and the organic azido group. The closed measuring system prevents the solutions from evaporating and gives a good adiabaticity. The amount of the solution weighed-in was about 6 g, the measuring cells used are made from titanium with one inch in diameter. All named energetic substances would deflagrate after a short period of controllable self heating with the weighed-in amount of energetic substance. The advantage of the investigation of the solutions is that the decomposition of the energetic substances can be followed in a fully controlled way. With the self heat rate curves one can distinguish the plasticizers and binders with respect to the decomposition temperature range, the heat generation and the heat generation rate. The Arrhenius parameters and the released heats of reaction have been determined from the self heat rate curves, which have been described well with reactions of first order. The self heat rate curves have been scaled to the thermal inertia equal to one, which corresponds to (1) the measurement on a solution without measuring cell and to (2) the measurement on the energetic substance alone without solvent and measuring cell. The procedures of the scaling and of the data evaluation are described. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Adiabatic self heating; Energetic plasticizer; Energetic binder; Decomposition kinetic parameters; Description of adiabatic self heat rate

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1. Introduction

Energetic plasticizers and binders developed or used during the last decade contain the following energetic groups: nitric acid ester group, nitramine group, azido group. The basic objectives of developing energetic binders and plasticizers are: (1) increase of the thermal stability, (2) increase in energy content, (3) adjustment of the oxygen balance in a formulation, (4) improvement of the plasticizer functions in formulations: reducing the glass transition temperature and the brittle–ductile transition temperature, reducing migration and the so-called exudation, improving

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of other mechanical properties of the propellant matrix and (5) the improvement of the burning behaviour of the propellant. Apart from the additional energy of the azido group, it is also interesting because of its high gas production rate (nitrogen release). This can increase the burning rate and intensify the effect of the blast waves of high explosives. The nitric acid ester group is known for its low thermal stability, experienced in common blasting oils and nitrocellulose. This has not changed in the newer binders and plasticizers, which contain it as the energetic group. The advantage is the different decomposition behaviour of the polymeric backbone compared to the one of nitrocellulose. As known so far, the azido group do not induce an autocatalytic decomposition.

Comparative investigations with regard to the decomposition triggered by thermal energy classifies the substances investigated here in terms of their thermal stability and the energy released in amount and per time respectively. The method used was the adiabatic self heating of toluene solutions determined by an 'accelerating rate calorimeter' (ARC^{TM}). The closed measuring system prevents evaporation. The advantage of performing the investigations using solutions is that the course of the decomposition reaction can be adjusted in its rate and therefore it can be measured in a controlled way and the reaction is more homogeneous. The energetic compounds alone in amounts used with the solutions would all deflagrate after a short controllable period of adiabatic self heating.

2. Apparatus

2.1. Principle of the method

A short description is presented here, a detailed one can be found in [1]. The main components of the ARC^{TM} made by Columbia Scientific Industries, Austin, TX, USA (recently taken over by Arthur D. Little, Cambridge, MA, USA) can be seen in Fig. 1.

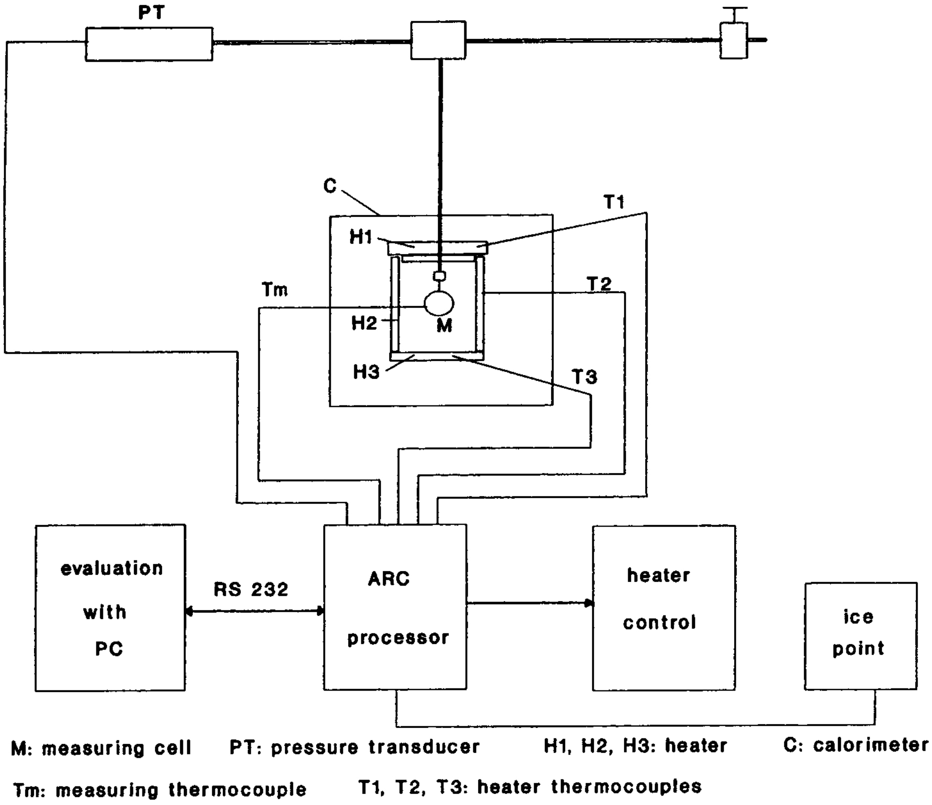

Fig. 1. Scheme of the ARC^{TM}.

The heating block contains three separate heaters H1, H2 and H3 which can be regulated individually using the heating block thermocouples T1, T2 and T3. The measuring cell is positioned in the center of the heating block. The spherical measurement cells with a connecting stem can be made from titanium or stainless steel or tantalum or Hastelloy C 276 with a diameter of one inch or 0.5 inches. The measuring cell thermocouple T_m is fixed to the measuring cell using a clip. All thermocouples are sheathed and of type N (Nisil/Nicrosil). The measuring cell has a connection to the pressure transducer (PT) by a thin (1/16 inch) high pressure capillary tube. The measurements are made on the closed system, which makes possible the adiabaticity of the measurement system. The measurement signals are transmitted to the ARC^{TM} processor, which executes the measuring program and controls the counter heating for the sample cell during the self heating of the sample. This counter heating generates a quasi-adiabatic environment. An electronic ice point device producing a zero centigrade bath is used as a temperature reference point for the thermocouples.

The course of the ARC^{TM} measurement in the mode 'heat-wait-search' is shown in Fig. 2. The wait period serves to equilibrate the sample and the measuring cell with the environment after heating to the start temperature or after heating by one heat step. During the search period the processor checks whether the sample shows a self heating. To do this, the changes in temperature of the measuring cell are compared with a preset sensitivity parameter. If the temperature increase per unit time exceeds this preset level over a period of time, determined by another parameter, this is recognized as the start of the self heating and the device switches to the exotherm mode and the processor starts the counter heating. If this preset level is not exceeded during the search period, the sample is heated by a heat step and this in turn is followed by another wait and search period. This process is repeated until an exotherm has been found or until a preset end temperature has been reached.

2.2. Taking the inert masses into consideration

During the exothermal decomposition, the sample also heats up the measuring cell itself. This means that the self heat rate is decreased by the so-called inert mass (means it show no own heat generation) of the measuring cell and other existing inert masses compared to a measurement without inert masses. To set up the heat balance equation, the increase in temperature at time t of the entire system 'measuring cell/sample' is called $\Delta T_{MS}(t) = T_{MS}(t) - T_{MS}(0)$ and that

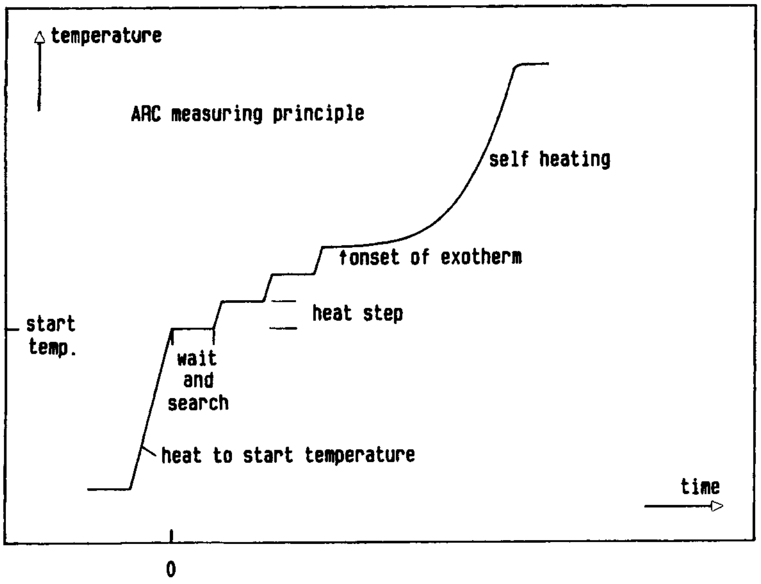

Fig. 2. ARC^{TM} measuring principle of the measuring mode 'heat-wait-search'.

of the simulated measurement on the sample alone is called $\Delta T(t) = T(t) - T(0)$ with $T_{\mathrm{MS}}(0) = T(0)$. During the self heating both the temperature differences change with time. The heat balance equation given in Eq. (1) takes into consideration the dependency on temperature of the specific heat capacities and the decomposition of the sample during the course of the reaction.

$$\left(\sum_i m_i(R(t)) \cdot c_{X,i}(T(t))\right) \cdot \Delta T(t) = \left(\sum_i m_i(R(t)) \cdot c_{X,i}(T(t)) + m_{\mathrm{M}} \cdot c_{X,\mathrm{M}}(T(t)) + \sum_j m_j \cdot c_{X,j}(T(t))\right) \cdot \Delta T_{\mathrm{MS}}(t). \tag{1}$$

The specific heat capacities c_X are thermodynamically complex because neither pressure nor volume are strictly constant. Actually used are the ones at constant pressure, c_P, because the changes in pressure are small, often below 10 bar, and this has nearly no effect on the intermolecular distances and intramolecular geometries in liquids and solids. The specific heat capacity at constant volume, c_V, would have to be used for gas reactions. $R(t)$ is the reaction coordinate or equivalently the degree of reaction conversion, which is used to determine the sample mass m_{S} ($=m_1$) and the masses of the reaction products m_i. The values with index M apply to the measuring cell, the sum expression over j includes additional thermally inert masses. Eq. (1) must be applied also before the onset of the measured exotherm, if there is already an appreciable decomposition.

In the case of an ARC$^{\mathrm{TM}}$ measurement without sample and decomposition product analysis, the course of the reaction with regard to $R(t)$ is unknown. But it is the point of interest in thermal analysis to get the information from the thermal data without the real chemical data on the decomposition of the sample. It is pointed out that this is not possible always. One has to check carefully the system under consideration, if thermal analysis is applicable in an unambiguous way.

To proceed with this method of thermal analysis, approximations are introduced. Only the sample mass m_{S} and the average specific heat capacity $c_{P,\mathrm{S}}$ are used and similar approximations are made for the other terms. The dependency on temperature is also not taken into consideration, as $\Delta T_{\mathrm{MS}}(t)$ is usually between 30°C and 70°C. The average value of $c_{P,\mathrm{S}}$ for organic substances is taken as 2.092 J/(g K). Eq. (2) is the simplified form of Eq. (1).

$$m_{\mathrm{S}} \cdot c_{P,\mathrm{S}} \cdot \Delta T(t) = \left(m_{\mathrm{S}} \cdot c_{P,\mathrm{S}} + m_{\mathrm{M}} \cdot c_{P,\mathrm{M}} + \sum_j m_j \cdot c_{P,j}\right) \cdot \Delta T_{\mathrm{MS}}(t). \tag{2}$$

Eq. (2) can be written as Eq. (3) with the abbreviation ϕ given in Eq. (4).

$$\Delta T(t) = \phi \cdot \Delta T_{\mathrm{MS}}(t), \tag{3}$$

$$\phi = 1 + \frac{m_{\mathrm{M}} \cdot c_{P,\mathrm{M}} + \sum m_j \cdot c_{P,j}}{m_{\mathrm{S}} \cdot c_{P,\mathrm{S}}}. \tag{4}$$

The quantity ϕ is called the thermal inertia of the system ‘sample/measuring cell’, in short named ϕ-factor. The ϕ-factor is used as a correction quantity, which means that the influence of the inert masses can be approximately eliminated [1]. A precise correction is possible using Eq. (1) and all the necessary experimental information.

3. Evaluation and scaling of the adiabatic self heat rate curves

3.1. Types of the adiabatic self heat rate curves

Fig. 3 shows typical adiabatic self heat rate curves $h(T)$ for different reactions. The adiabatic self heat rates $h(T)$ shown in Fig. 3 and in the following figures are presented as lg(h[°C/min]) against $1/T$ [1/K]. On the abscissa the temperature values are indicated in °C. The Arrhenius parameters used to calculate the curves in Fig. 3 without the autocatalytic curve are the ones not in brackets given in Fig. 3. The onset temperature T_0 of the self heating is 150°C and its final temperature $T_{\mathrm{f}} = 250$°C. The curves have been calculated for $\phi = 1$, that means for a simulated measurement without measuring cell or for a measurement with negligible influence by inert masses.

In the case of a reaction of zero order, $h(T)$ results in a straight line, which ends at T_{f} because of the consumption of the substance. For reactions of first,

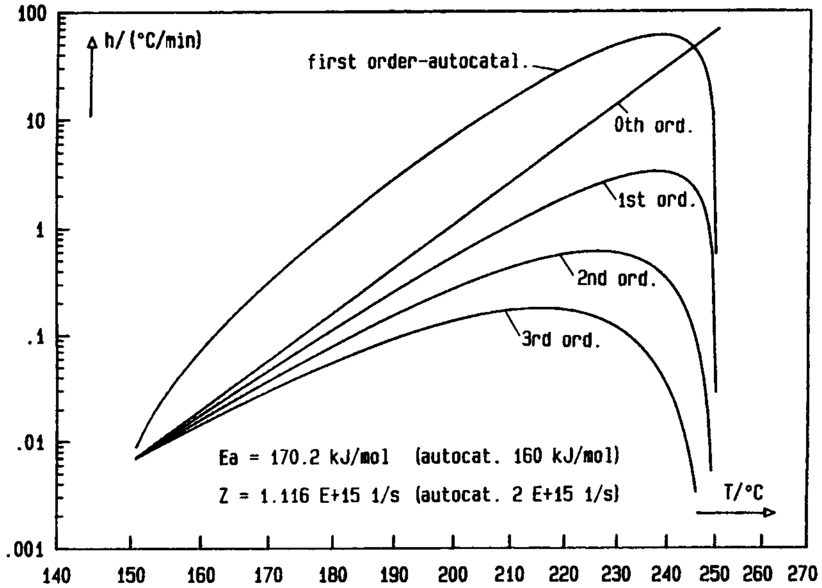

Fig. 3. Types of adiabatic self heat rate curves originating from decomposition reactions with different order n and of an autocatalytic reaction.

second and third order, the $h(T)$-curves pass a maximum and then return to zero when they have reached T_f. The higher the reaction order n, the wider the range of the maximum of the curve. The $h(T)$-curves with $n\neq 0$ lie below the curve with $n=0$. The curves clearly show that the order of reaction can be determined definitely. Fig. 3 also shows the course of $h(T)$ for an autocatalytic reaction according to the reaction scheme Eq. (5) and to the kinetic expression Eq. (6), with $\Delta H_{R,i}$ as reaction enthalpies. See also Eqs. (12) and (13).

$$\begin{array}{ll} \mathrm{A}\xrightarrow{k_{A1}}\mathrm{B}+\mathrm{Z} & \Delta H_{\mathrm{R},1}\\ \mathrm{A}+\mathrm{B}\xrightarrow{k_{A2}}2\,\mathrm{B}+\mathrm{Z} & \Delta H_{\mathrm{R},2}\end{array} \tag{5}$$

$$\begin{aligned}\frac{\mathrm{d}A(T(t))}{\mathrm{d}t} &= -k_{A1}(T(t))\cdot A(T(t))\\ &\quad - k_{A2}(T(t))\cdot A(T(t))\cdot B(T(t))\end{aligned} \tag{6}$$

The primary decomposition of A with the reaction rate constant k_{A1} includes the formation of the autocatalytically effective product B by a reaction of first order with the Arrhenius parameters used for the other curves in Fig. 3. The second decomposition reaction is the autocatalytic reaction. The reaction rate constant k_{A2} has the Arrhenius parameters given in brackets in Fig. 3.

3.2. Determination of Arrhenius parameters from adiabatic self heating

To determine the Arrhenius parameters of the reaction rate constant $k(T)$ of the decomposition reaction, the consumption of the substance as a function of temperature and time is the necessary information. If the decomposition of the substance A follows a defined reaction, the reaction rate constant can be determined from the self heat rate using the appropriate kinetic expression and balancing the substance consumption (=degree of reaction conversion) and the temperature increase, Eq. (7). The increase in temperature is equivalent to the released heat Q_A by the decomposition reaction. The same approximations that are used in Eq. (2) are used here too. In Eq. (7) the terms '$m_K\cdot C_K$' (thermal masses) have been eliminated already. The onset quantity $Q_A(T(t_0))$ is normally set to zero. In Eq. (7) the ΔT and the ΔT_{MS} are not functions of time.

$$\begin{aligned}\frac{A(t,T)}{A(0)} &= \frac{A(T(t))}{A(T(0))} = A_r(T(t))\\ &= \frac{Q_A(T(t_f)) - Q_A(T(t))}{Q_A(T(t_f)) - Q_A(T(t_0))} = \frac{T_f - T(t)}{\Delta T}\\ &= \frac{T_{fMS} - T_{MS}(t)}{\Delta T_{MS}}.\end{aligned} \tag{7}$$

$A(T(t))$ is the amount of sample substance A (concentration or mass) at time t at temperature $T = f(t)$; $A(T(0))$ is the amount of substance A at $T(0)$, the onset temperature of the adiabatic self heating; $T(0)$ is also named T_0 or $T(t_0)$; $T(t)$ is the temperature of the sample alone at time t at condition $\phi = 1$; $T_{\mathrm{MS}}(t)$ is the temperature of the system 'sample/measuring cell' at time t at $\phi \neq 1$; ΔT is the adiabatic temperature increase $\Delta T = T_{\mathrm{f}} - T(0)$ of the sample alone at condition $\phi = 1$; ΔT_{MS} is the adiabatic temperature increase $\Delta T_{\mathrm{MS}} = T_{\mathrm{fMS}} - T_{\mathrm{MS}}(0)$ of the system 'sample/measuring' cell at $\phi \neq 1$; T_{f} is the final temperature of the adiabatic self heating of the sample alone at condition $\phi = 1$; T_{fMS} is the final temperature of the adiabatic self heating of the system 'sample/measuring cell' at condition $\phi \neq 1$.

The differentiation of Eq. (7) gives Eqs. (8a) and (8b), where Eq. (8b) is the normalized form with $A_{\mathrm{r}}(T(t)) = A(T(t))/A(T(0))$.

$$\begin{aligned}\frac{\mathrm{d}A(T(t))}{\mathrm{d}t} &= -\frac{A(T(0))}{\Delta T}\cdot\frac{\mathrm{d}T(t)}{\mathrm{d}t}\\ &= -\frac{A(T(0))}{\Delta T}\cdot h(T(t))\\ &= -\frac{A(T(0))}{\Delta T_{\mathrm{MS}}}\cdot h(T_{\mathrm{MS}}(t)). \qquad (8a)\end{aligned}$$

$$\begin{aligned}\frac{\mathrm{d}A_{\mathrm{r}}(T(t))}{\mathrm{d}t} &= -\frac{1}{\Delta T}\cdot h(T(t))\\ &= -\frac{1}{\Delta T_{\mathrm{MS}}}\cdot h(T_{\mathrm{MS}}(t)). \qquad (8b)\end{aligned}$$

The combination of Eq. (8b) with a reaction kinetic expression, here a reaction of order n shown in Eq. (9) and in normalized form in Eq. (10), gives Eqs. (11a) and (11b) for the adiabatic self heat rate $\mathrm{d}T(t)/\mathrm{d}t = h(T(t))$ at the two conditions $\phi = 1$ and $\phi \neq 1$:

$$\frac{\mathrm{d}A(T(t))}{\mathrm{d}t} = -k_n(T(t))\cdot A^n(T(t)). \qquad (9)$$

$$\begin{aligned}\frac{\mathrm{d}A_{\mathrm{r}}(T(t))}{\mathrm{d}t} &= -k_{n,\mathrm{r}}(T(t))\cdot A_{\mathrm{r}}^n(T(t)) \text{ with } k_{n,\mathrm{r}}(T(t))\\ &= k_n(T(t))\cdot A^{n-1}(T(0)). \qquad (10)\end{aligned}$$

$$h(T(t)) = k_{n,\mathrm{r}}(T(t))\cdot\Delta T\cdot\left(\frac{T_{\mathrm{f}} - T(t)}{\Delta T}\right)^n \quad \text{with } \phi = 1. \qquad (11a)$$

$$h(T_{\mathrm{MS}}(t)) = k_{n,\mathrm{r}}(T(t))\cdot\Delta T_{\mathrm{MS}}\cdot\left(\frac{T_{\mathrm{fMS}} - T_{\mathrm{MS}}(t)}{\Delta T_{\mathrm{MS}}}\right)^n \quad \text{with } \phi \neq 1. \qquad (11b)$$

With Eqs. (11a) and (11b) the reaction rate constants $k_{n,\mathrm{r}}(T)$ can be determined just by arithmetic operations on the measured adiabatic self heat rate $h(T)$. Eq. (11a) was used to calculate the curves in Fig. 3 with $n = 1, 2, 3$. In a reaction of first order, $h(T)$ is explicitly independent of $A(T(0))$ but implicitly dependent on $A(T(0))$, because T_{f} increases with increasing amount of $A(T(0))$. To calculate the autocatalytic self heating in Fig. 3, the reaction kinetic scheme according to Eq. (5) was taken as formulated in Eq. (12), using $B(T(t)) = A(T(0)) - A(T(t))$.

$$\begin{aligned}\frac{\mathrm{d}A_{\mathrm{r}}(T(t))}{\mathrm{d}t} &= -k_1(T(t))\cdot A_{\mathrm{r}}(T(t))\\ &\quad -k_2(T(t))\cdot A_{\mathrm{r}}(T(t))\cdot(1 - A_{\mathrm{r}}(T(t)))\\ &\quad \text{with } k_1(T(t)) = k_{A1}(T(t))\\ &\quad \text{and } k_2(T(t)) = k_{A2}(T(t))\cdot A(T(0)) \qquad (12)\end{aligned}$$

Eq. (13) is gained by combining Eq. (12) with Eq. (8b) and using Eq. (7) to substitute $A_{\mathrm{r}}(T(t))$. With this approximation the autocatalytic self heat rate curve in Fig. 3 was calculated.

$$\begin{aligned}h(T(t)) &= k_1(T(t))\cdot(T_{\mathrm{f}} - T(t)) + k_2(T(t))\\ &\quad\cdot(T_{\mathrm{f}} - T(t))\cdot\left(1 - \frac{T_{\mathrm{f}} - T(t)}{\Delta T}\right). \qquad (13)\end{aligned}$$

3.3. Scaling of the experimental adiabatic self heat rate curves to $\phi=1$

The scaling of the adiabatic self heat rate curves will be exemplified with the adiabatic self heating of non-cured GAP alone (ICT, batch 1 in Table 2) and the solution of this GAP in dioxan.

3.3.1. Data used to show the scaling procedure

Fig. 4 shows the adiabatic self heat rates of GAP alone and GAP dissolved in toluene and in dioxan (about 10 mass% of GAP in both solvents). The curves of the solutions have a defined final temperature T_{fMS}. GAP alone shows a transition to deflagration after the controllable part of the self heating as do other explosive substances [2]. The rate determining first reaction step of the GAP decomposition is assumed to be the formation of molecular nitrogen from the azido group, C–N–N ≡ N1. This mechanistic model is supported by

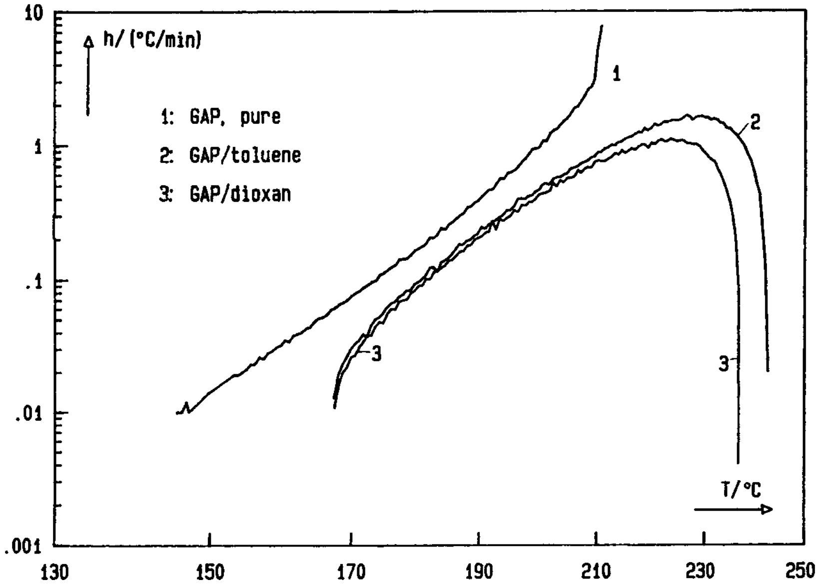

Fig. 4. Adiabatic self heat rates of uncured GAP and of uncured GAP dissolved in toluene and dioxan with 10 mass% content.

(1) the corresponding bond energy [3,4,5–7], (2) the mass spectrometric investigation of nitrogen production [8], (3) thermoanalytical investigations [9] and previous investigations on alkylazides, see Table 1. The activation energy of the azido group decomposition or of the GAP decomposition should therefore be approximately equal to the bond energy of the $RN–N_2$ bond, which is given at 163.2 kJ/mol in [4] and at 170 kJ/mol in [7].

The activation energies determined from the ARC^{TM} measurements agree well with the bond energy of the $RN–N_2$ bond and with the values stated in the litera-

Table 1
Arrhenius parameters of the decomposition of GAP, determined by different methods. m_S is sample mass, T_0 is onset temperature

Method	Ref.	m_S (mg)	T_0 (°C)	Temperature range (°C)	E_a (kJ/mol)	Z (s^{-1})	lg Z (s^{-1})
N_2-formation, mass spectrometry	[8]	ca. 25	ca. 120	140–170	176.6	n.m.	n.m.
DTA-measurements (heat rate to peak temp.)	[9]	n.m. (2)	ca. 190	220–260	174.0	n.m.	n.m.
Isothermal TGA	[10]	1.5–2.5	ca. 170	180–205	164.9	1.26×10^{14}	14.1
Non-isothermal TGA	[10]	1.5–2.5	ca. 170	180–220	164.9	6.31×10^{13}	13.8
Mass loss/FTIR	[10]	0.2–0.8	ca. 240	240–260	177.0	1×10^{19}	19.0
NH_3-formation/FTIR[a]	[11]	n.m. (5)	ca. 165	165–260	170.7	3.548×10^{15}	15.55
Isothermal TGA	[12]	ca. 1	ca. 170	170–240	135.7[b]	8.78×10^{13}	13.9
ARC, GAP/toluene	[2]	592	167	175–230	168.9	7.814×10^{14}	14.89
ARC, GAP/dioxan	[2]	612	167	175–230	170.2	1.116×10^{15}	15.05
$CH_3–N_3$	[13]	(120)	(155)	155–200	170.7	2.85×10^{14}	14.455
$C_2H_5–N_3$	[14]	(100–600)	(187)	187–230	167.8	3.30×10^{14}	14.519
n-Propyl–N_3	[14]	(100–700)	(190)	190–226	164.9	1.48×10^{14}	14.169
iso-Propyl–N_3	[14]	(100–700)	(190)	190–223	161.1	7.20×10^{13}	13.857

n.m.: not mentioned in reference, values in brackets are estimated.

[a] The monitored reaction sequence is probably the elimination of the acid HN_3 and the consecutive rate determining step of its decomposition into NH and N_2, which has a similar activation energy as the splitting reaction in $C–N–N_2$. NH forms then NH_3 by H abstraction.

[b] The low activation energy may reflect the influence of evaporation.

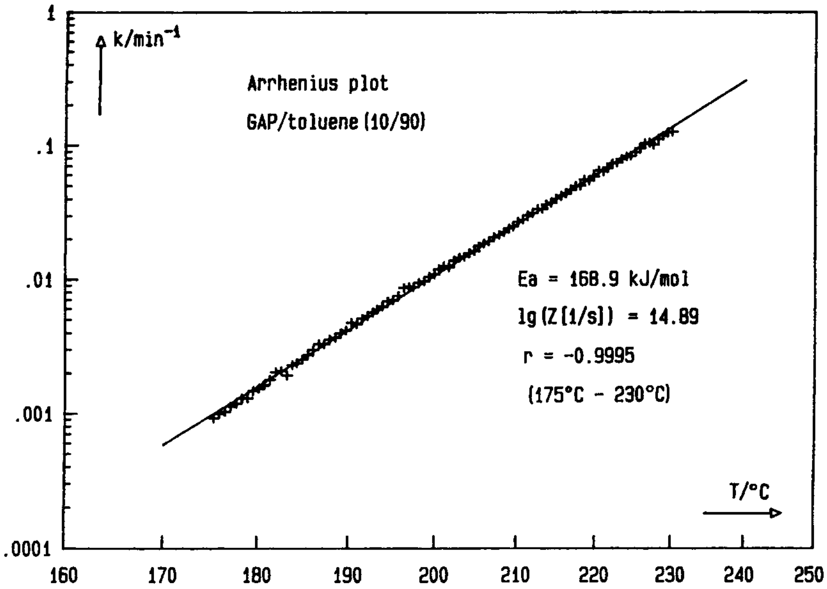

Fig. 5. Arrhenius plot of the GAP decomposition in toluene solution.

ture listed in Table 1. The corresponding Arrhenius plots are shown in Figs. 5 and 6. The obtained correlation coefficients are >0.999. The Arrhenius parameters determined from investigations of the unimolecular decomposition of the azido group of the gaseous azides, methylazide and ethylazide [13,14] represent the activation energy of the rate determining reaction step. The decrease in activation energy by increasing positive inductive effect of the alkyl group indicates a stabilization of the nitrene functionality analogously to the stabilization of the radical functionality.

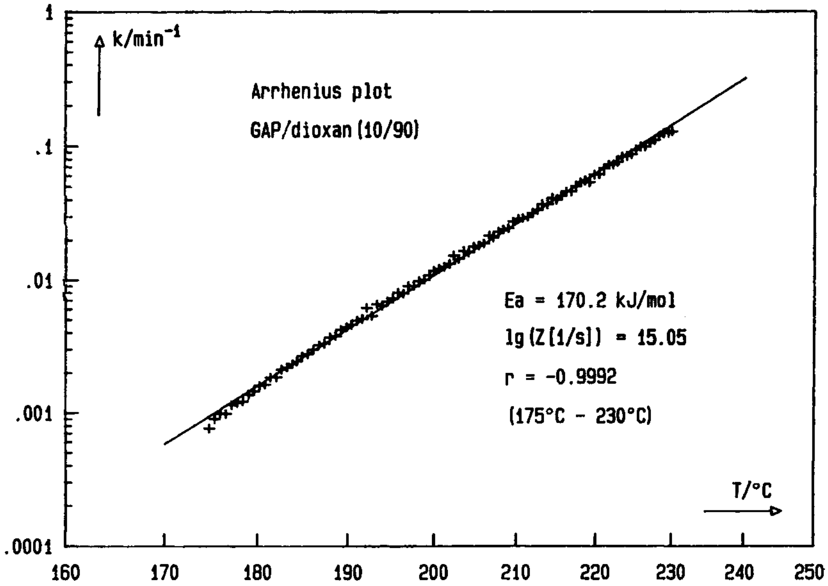

Fig. 6. Arrhenius plot of the GAP decomposition in dioxan solution.

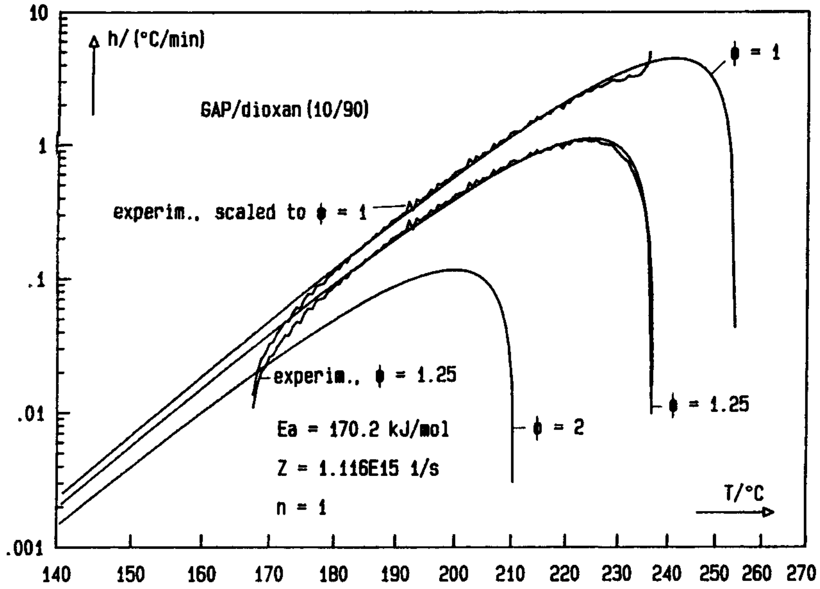

Fig. 7. Scaling of the adiabatic self heat rate of the GAP/dioxan solution to the ϕ-factors $\phi_1 = 1$ and $\phi_1 = 2$, smooth curves. The measured curve with $\phi = 1.25$ has a noise pattern. It is described also at $\phi = 1.25$, smooth curve. The experimental data have been scaled to $\phi_1 = 1$ too, which is the curve with noise pattern on the scaled smooth curve with $\phi_1 = 1$.

The consecutive stabilizing reactions of the nitrene formed by the loss of nitrogen in the C–N_3-group are very fast due to the high reactivity of the nitrene, which performs intramolecular and intermolecular insertion reactions in neighbouring chemical bonds. A polymerization by an imine functionality may also occur. It is also possible that the loss of nitrogen from the C–N_3-group and the insertion take place in a concerted or concomitant way [6]. The existence of intermolecular insertion reactions of GAP is supported by the following observations: (1) the formation of an insoluble residue during the hydrolytic treatment of the cured GAP-binder and of GAP bonded propellants [15], (2) the appearance and the increase of an insoluble part with the ageing of uncured GAP and (3) the shift of the glass transition temperature determined by DMA with the ageing of the cured GAP-binder [16].

3.3.2. Description of the scaling procedure

It will be shown that it is possible to scale the self heat rate curve of the GAP solution in such a way that it represents the self heating measured from GAP alone. This behaviour makes it possible to scale the measured data to $\phi = 1$ also, which means that no thermally inert mass is heated and therefore the adiabatic self heating of the energetic substance alone is simulated with the data of the measurements on the solutions. The scaling of the $h(t)$-data obtained from solutions was applied in [1] also but not compared to the $h(t)$-data of the substance alone.

Fig. 7 shows three sets of curves. The curve with a noise pattern in the middle is the measured adiabatic self heat rate of GAP/dioxan solution (10 mass% GAP) with a ϕ-factor for the solution of value 1.25. The self heat rate curve $h(T)$ calculated according to Eqs. (11a) and (11b) with $n = 1$ (which gives Eq. (13)) and with $\phi = 1.25$ can be seen also as the curve without noise pattern. From the start temperature of 175°C on for the data evaluation, this calculated curve agree very well with the measured data. The calculated curve has been extrapolated down to 140°C. More concentrated solutions have lower experimental onset temperatures T_0.

Using Eqs. (11a) and (11b), $h(T)$ can also be calculated for other ϕ-factors. With the factors ϕ_1 and ϕ_2, Eqs. (14) and (15) are formulated for the entire measurement system, but omitting the index MS for reasons of better reading.

$$h_1(T(t)) = k_{n,\mathrm{r}}(T(t)) \cdot \Delta T_1 \cdot \left(\frac{T_{\mathrm{f}1} - T_1(t)}{\Delta T_1}\right)^n, \tag{14}$$

$$h_2(T(t)) = k_{n,\mathrm{r}}(T(t)) \cdot \Delta T_2 \cdot \left(\frac{T_{\mathrm{f}2} - T_2(t)}{\Delta T_2}\right)^n. \tag{15}$$

According to Eq. (3), the following applies for the relation between the two temperature differences ΔT_i (exactly $\Delta T_{\mathrm{MS},i}$), the two final temperatures $T_{\mathrm{f},i}$ (exactly $T_{\mathrm{fMS},i}$) and the onset temperatures $T_i(0)$ (exactly $T_{\mathrm{MS},i}(0)$), Eq. (16).

$$\Delta T = \phi_1 \cdot \Delta T_1 = \phi_2 \cdot \Delta T_2, \quad \phi_1 \cdot (T_{\mathrm{f}1} - T_1(0)) = \phi_2 \cdot \Delta T_2,\ T_{\mathrm{f}1} = \frac{\phi_2}{\phi_1}\Delta T_2 + T_1(0). \tag{16}$$

The temperature difference ΔT is the adiabatic temperature rise of the sample alone. Differences in the ϕ-factor result only by the different inert masses. Combining Eqs. (14) and (16) the simulated self heat rate $h_1(T)$ can be calculated from the measured self heat rate $h_2(T)$ with Eq. (17). The non-indexed temperature $T(t)$ in Eqs. (17) and (18) is the running variable.

$$h_1(T(t)) = k_{n,\mathrm{r}}(T(t))\frac{\phi_2}{\phi_1}\Delta T_2 \times \left(\frac{(\phi_2/\phi_1)\Delta T_2 + T_1(0) - T_1(t)}{(\phi_2/\phi_1)\Delta T_2}\right)^n \quad \text{with}\ T_1(t) \cong T(t) \tag{17}$$

To use Eq. (17) the reaction rate constant is determined first from the experimental data that means from the $h_2(T)$-curve. Then the calculated data are scaled to other ϕ-factors according to Eq. (17). The 'theoretical' self heat rate curves shown in Fig. 7 of virtual solutions of GAP with $\phi_1 = 1$ and $\phi_1 = 2$ have been calculated using Eq. (17). The increase of the ϕ-factor from 1.25 to 2 reduces the measurable self heat rate considerably.

The experimental values itself can also be scaled to $\phi_1 = 1$. The appropriate equation is arrived at by dividing Eq. (14) by Eq. (15) and inserting the expressions from Eq. (16), which results in Eq. (18).

$$\frac{h_1(T(t))}{h_2(T(t))} = \frac{\phi_2}{\phi_1} \times \left(\frac{(\phi_2/\phi_1)\Delta T_2 + T_1(0) - T_1(t)}{T_{\mathrm{f}2} - T_2(t)} \cdot \frac{1}{\phi_2/\phi_1}\right)^n$$

with the following equalities and definition

$$T_1(0) = T_2(0), T_1(t) = T_2(t) \cong T(t) \tag{18}$$

With Eq. (18) the experimental curve $h_2(T)$ is scaled to $h_1(T)$ with the factor ϕ_1.

In Fig. 7 one can see the scaled experimental curve of the GAP/dioxan solution according to Eq. (18) at $\phi_1 = 1$ as the curve with a noise pattern coinciding with the $h(T)$-curve calculated with Eq. (17) for the condition $\phi_1 = 1$. Deviations occur when $T(t)$ is greater than T_M, the temperature of the maximum of the experimental adiabatic self heat rate curve $h_2(T)$, as then $h_2(T)$ tends towards zero very quickly and a high scattering occurs in the experimental curve scaled to $\phi_1 = 1$. Non-existing measurements cannot be constructed so that the scaled experimental curve seems to be incomplete compared to the full theoretical curve at $\phi_1 = 1$ and to the experimental curve at $\phi = 1.25$.

The adiabatic self heat rate curve of GAP alone (Fig. 4) has approximately the same slope in the middle part as the curves of the GAP solutions, which indicates at least a similar activation energy for the decomposition of GAP alone. The experimental ϕ-factor of the GAP solutions is 12.5 in relation to the weighed-in GAP. In contrast to the GAP solutions, pure GAP deflagrates under the measurement conditions stated at an experimental ϕ-factor of 6.2. Fig. 8 shows the theoretical $h(T)$-curves determined with the experimental curve of the GAP/dioxan solution as reference data and using Eq. (17) with $\phi_1 = 12.5$, $\phi_1 = 6.2$ and $\phi_1 = 1$. The curve with $\phi_1 = 1$ is equivalent to a 'solution with 100% GAP', i.e. pure GAP without any thermally inert mass. The expression 'solution with 100% GAP' points to the fact that the decomposition takes place in the same way as it does in solution, that means homogeneous and without deflagration. The experimental data of the GAP/dioxan solution, now with reference to the GAP content of the solution, are described very well by Eq. (17), as it was the case with the reference to the solution itself, see Fig. 7. The measured data of GAP

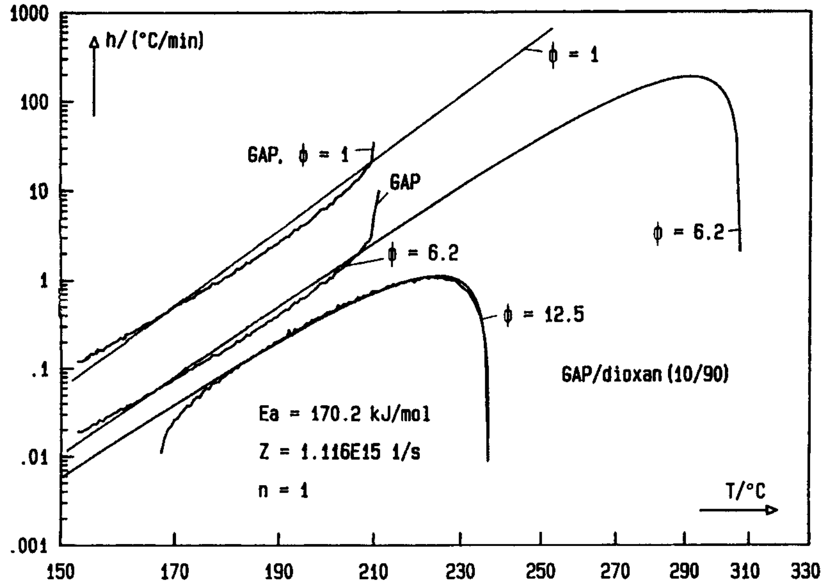

Fig. 8. Scaling of the adiabatic self heat rate of GAP dissolved in dioxan to $\phi_1 = 6.2$ and $\phi_1 = 1$, both curves are smooth. The solution type curve with a noise pattern is the experimental curve with a ϕ-factor equal to 12.5 with regard to the GAP content. It is also described at $\phi_1 = 12.5$, smooth curve. The measured data of uncured GAP alone have $\phi = 6.2$ and are scaled to $\phi_1 = 1$, these both curves have a noise pattern.

alone with $\phi = 6.2$ are positioned well on the calculated *h*(*T*)-curve with $\phi_1 = 6.2$ (using Eq. (17)), and the measured data scaled to $\phi_1 = 1$ are equally well described by the theoretical *h*(*T*)-curve 'solution with 100% GAP' with $\phi_1 = 1$.

The deviation of the experimental GAP curve from the theoretical curve with $\phi_1 = 6.2$ is explainable. Some of the GAP has been condensed in the vertical connection tube of the pressure capillary line to the pressure transducer, so the actual ϕ-factor has been increased somewhat during the measurement. This is expressed in the figure by a shift of the experimental GAP curve below the theoretical curve at increased temperatures. In the case of the solutions the vertical connection tube may act as a reflux condenser.

The conclusion is the measured data of GAP alone and the measured data of GAP in the dioxan solutions agree well by the scaling with the associated ϕ-factors. This is the argument to use the experimental data of solutions of the energetic substances to get information on the decomposition behaviour of the energetic substances alone. The decomposition of the discussed binders and plasticizers in the propellant matrix can be assumed to be a homogeneous one, because with such substances the decomposition is statistically distributed in the propellant.

4. Substances investigated and measuring conditions

The adiabatic self heating was measured from the following plasticizers and uncured binders with an ARC$^{\mathrm{TM}}$:

- mixture (58.8/41.2 in mass%) *N*-methyl-/*N*-ethyl-NENA (Me/Et-NENA) from ICI/USA, NENA means *N*-(2-nitratoethyl)-nitramine
- DANPE, 1,5-diazido-3-nitraza-pentane, from Rockwell
- GAPA, short chain GAP with N_3-end groups instead of OH, from Rockwell
- EGBAA (technical name A17), ethylene glycol-bis-(α-azidoacetate), from ICT
- Octylazide, from ICT, as model substance, not intended for use in explosives
- GAP-AA-2000, GAP with α-azidoacetic acid esterified OH-end groups, from ICT

- GAP-AA-500, as GAP-AA-2000, however short chains, from ICT
- uncured PolyGLYN, (also named PG in USA), poly-glycidylnitrate, from ICI/UK
- uncured GAP, poly-glycidylazide, from SNPE
- uncured GAP, poly-glycidylazide, from ICT

ICI/USA	ICI Explosives USA, Tamaqua, PA, USA
ICT/UK	ICI Explosives, Nobel's Explosive, Stevenston, Ayrshire, UK
SNPE	Société Nationale des Poudres et Explosivs, Vert-le-Petit, France
ICT	Fraunhofer-Institut für Chemische Technologie, Pfinztal, Germany
Rockwell	Rocketdyne Division, Rockwell International, Canoga Park, CA, USA

The substances were used as delivered. GAP and PolyGLYN are formally poly-(1,2-propylene glycol) or poly-(1,2-propylene oxide) with the energetic group attached to the lateral CH_3-group. Three types of energetic groups are represented with these compounds: the organic nitric acid ester group (NENA, PolyGLYN), the nitramine group (NENA, DANPE) and the organic azido group (in all but NENA and PolyGLYN). The substances were investigated as solutions in toluene p.A. grade with about 10 mass% contents of the energetic substances.

The amount of weighed-in toluene solution was between 5.8 and 6.7 g, which means an amount of energetic substance between 0.59 and 0.67 g. Such amounts give a high measuring sensitivity with the ARC^{TM}. Because of the higher sample amounts usable with the ARC^{TM} compared to a DSC apparatus, the sensitivity of an ARC^{TM} is higher by a factor of about 100–1000. Together with the somewhat varying measurement cell masses, thermal inertia values between 1.21 and 1.27 for the solutions were determined as well as between 12.0 and 12.7 for the pure energetic substances. Therefore the measurement conditions can be seen as identical for all substances in the meaning that the small differences in the experimental ϕ-factor do not change the course of the decomposition reactions. The measuring cells have been spherical containers made from titanium with one inch in diameter.

5. Results and discussion

Fig. 9 shows an overview of the measured adiabatic self heat rate curves of the substances investigated. Because of cross over in the curves, GAP-AA-500, GAP (ICT) and octylazide can be seen in Fig. 10

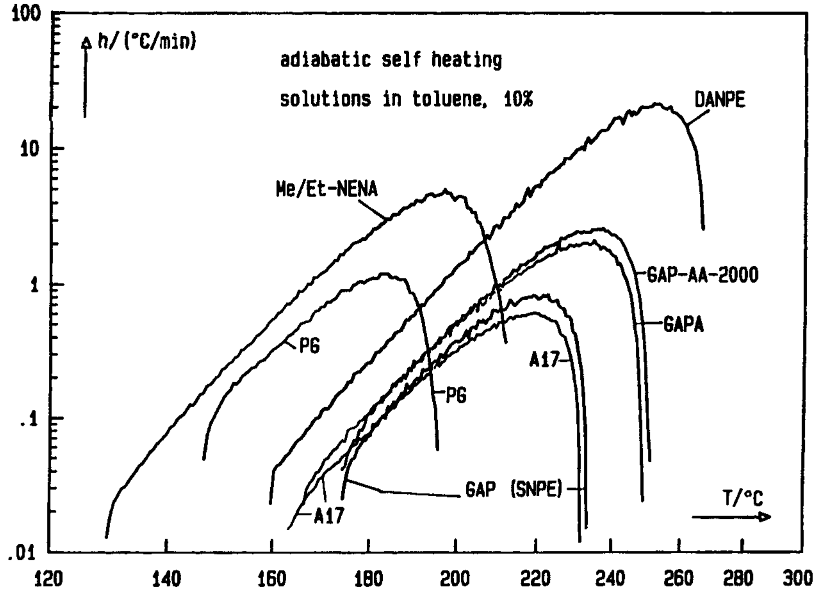

Fig. 9. Adiabatic self heating of plasticizers and uncured binders, measured in solutions of toluene with 10 mass% content, part 1.

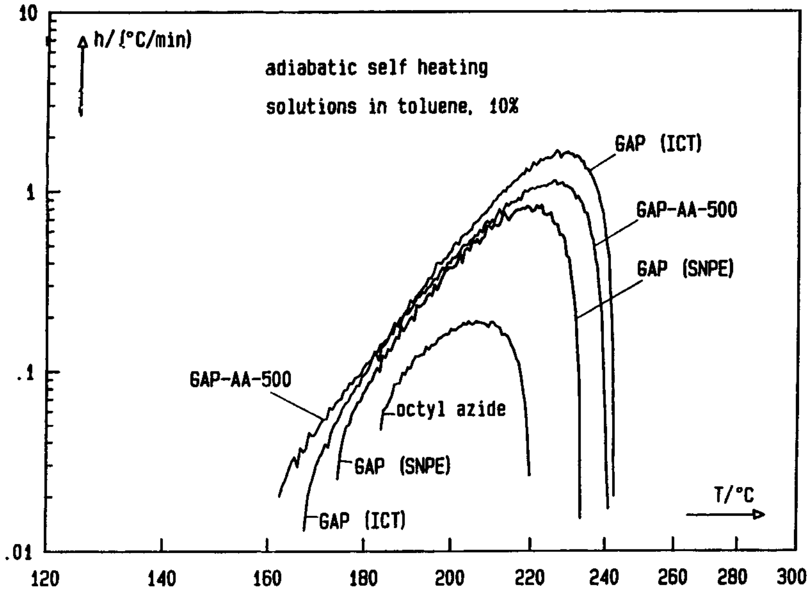

Fig. 10. Adiabatic self heating of plasticizers and uncured binders, measured in solutions of toluene with 10 mass% content, part 2.

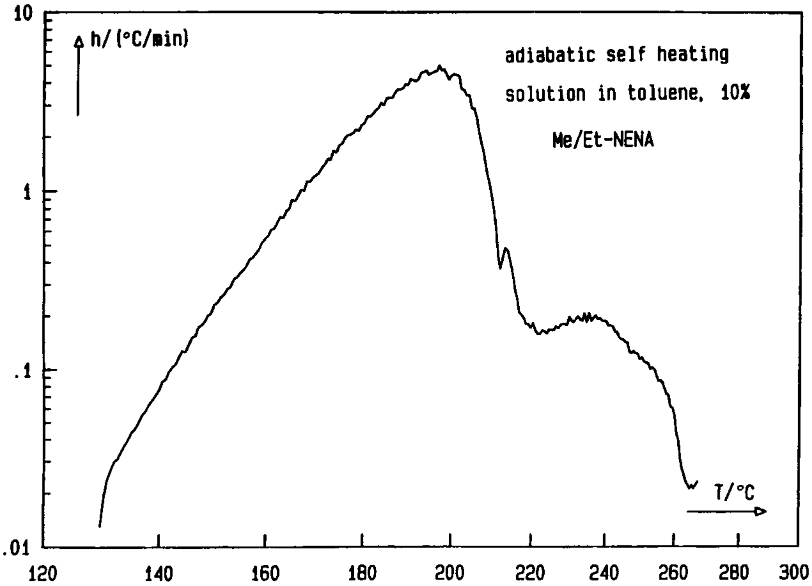

Fig. 11. Complete adiabatic self heat rate curve of Me-/Et-NENA, measured in solution of toluene with 10 mass% content.

together with GAP (SNPE). No smoothing was applied to the data obtained from the ARC^{TM}. The figures give a first information on (1) the temperature range of the decomposition and (2) from the maximum values of the self heat rate curves and from their 'curve widths' (temperature range) qualitatively on the released energies. It was possible to describe the overall decomposition reaction for all substances with a reaction of first order. A significant secondary reaction was found in the case of Me/Et-NENA. The other substances did not show any or only negligible secondary reactions. Fig. 11 shows the entire adiabatic self heat rate curve for Me/Et-NENA. Presumably, the second reaction is the decomposition of the nitramine group in connection with the residual part of the already decomposed nitric acid ester group. In this case only the first reaction range has been evaluated, which is associated to the decomposition of the nitric acid ester group. The onset temperature of decomposition was between 159°C and 174°C for the azido compounds, in the case of the nitric acid ester groups it was 130°C for Me/Et-NENA and 146°C for PolyGLYN. In order to remove the remaining influences of differing sample amounts and differing ϕ-factors on the evaluation of the data, the self heat rate curves were normalized to $\phi = 1$ with regard to the energetic substance alone, see Table 2. If solutions are considered, they are normalized to $\phi = 1$ with regard to the solution and to the weighed-in amount of the energetic substance. Fig. 12 shows the self heat rate curves scaled to $\phi = 1$ in relation to the solution of some of the substances. In the main, the sequence of the curves in this $h(T)$-graph is the same as the one in the graph of the experimental curves, because of nearly the same experimental conditions. However, in the case of substances, which show a similar experimental adiabatic self heat rate, it is possible that the sequences are reversed by the normalization, for example in the case of GAPA compared to GAP-AA-2000.

The characteristic experimental data are listed in Table 2. T_0 and h_0 are the onset data of the adiabatic self heating, T_M and h_M are the values of the maximum of the $h(T)$-curve and T_f its final temperature. Further data are listed in Table 2 on the Arrhenius parameters for the overall decomposition reactions of first order, on the released energies and on the adiabatic self heatings at $\phi = 1$ with regard to the energetic substances, such as the associated temperatures predicted for given adiabatic self heat rates h. The deviations given for the Arrhenius parameters and the correlation coefficients reflect the standard deviations of the measured data from the curves obtained according to Eq. (11b) with $n = 1$ transformed to the Arrhenius representations. The activation energies are between 157 and 169.4 kJ/mol for azido compounds. Me/Et-NENA and PolyGLYN have activation energy values of 165.1 and 166.8 kJ/mol respectively. The correlation coefficients of all Arrhenius plots are greater than 0.99. The values of the activation energies lie in the range of the bond energy of the CN–NN bond (161–170 kJ/mol) of the azido group and of the CO–NO_2 bond (160–170 kJ/mol) of the nitric acid ester group.

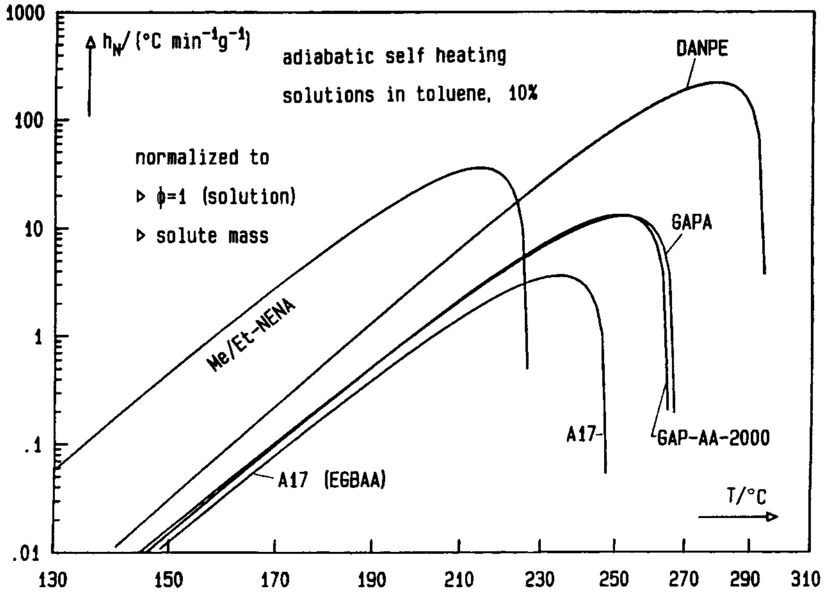

Fig. 12. Calculated adiabatic self heat rate curves of some of the investigated compounds, scaled to $\phi = 1$ and normalized to the amount of weighed-in energetic substance.

Table 2
Characteristic data of the adiabatic self heating of plasticizers and binders from the measurements on their solutions in toluene, Arrhenius parameters of the decomposition, released heats Q_A and data for curves scaled to a thermal inertia $\phi = 1$ with regard to the energetic substances alone

	GAP lot 1 ICT	GAP lot 2 ICT	GAP SNPE	EGBAA (A17) ICT	GAP-AA-2000 ICT	GAP-AA-500 ICT	Octylazide ICT	Me/Et-NENA ICI	PolyGlyn ICI	DANPE USA	GAPA USA
Amount solution (g)	5.920	6.744	5.883	6.005	6.001	6.002	6.003	6.006	5.988	6.143	6.215
Sample (g)	0.592	0.681	0.591	0.595	0.612	0.597	0.600	0.596	0.596	0.613	0.615
ϕ-solution	1.25	1.24	1.27	1.26	1.22	1.27	1.22	1.21	1.21	1.27	1.26
ϕ-sample	12.5	12.3	12.6	12.7	12.0	12.7	12.2	12.2	12.2	12.7	12.7
T_0 (°C)	167.4	169.9	174.3	161.4	174.1	162.3	177.6	129.6	146.7	159.0	166.3
h_0 (°C/min)	0.013	0.017	0.025	0.013	0.041	0.020	0.026	0.013	0.049	0.028	0.023
T_M (°C)	229.3	227.6	218.7	218.4	237.1	225.9	205.9	196.9[a]	183.4	251.4	234.7
h_M (°C/min)	1.63	1.55	0.82	0.598	2.62	1.14	0.188	5.00[a]	1.19	21.50	2.12
T_f (°C)	242.5	242.6	233.1	231.5	253.4	243.1	219.7	211.8[a]	205.5	266.4	249.1
Arrhenius parameters and released heats Q_A calculated from the self heat rate curves											
E_a (kJ/mol)	168.9±0.6	167.7±0.5	169.4±0.9	162.2±0.5	162.4±0.4	154.6±0.4	157.0±1.2	165.1±0.4	166.8±0.7	167.3±0.2	157.9±0.4
Z (s^{-1})	7.814E14	6.106E14	9.005E14	1.340E14	1.482E14	1.926E13	2.899E13	1.449E16	2.042E16	9.903E14	4.534E13
lg Z (s^{-1})	14.89±0.06	14.79±0.05	14.95±0.10	14.13±0.05	14.17±0.05	13.28±0.04	13.46±0.13	16.16±0.05	16.31±0.07	14.996±0.02	13.66±0.04
Correlation coefficient	0.9995	0.9995	0.9988	0.9996	0.9996	0.9997	0.9984	0.9996	0.9996	0.9999	0.9996
Q_A (J/g)	1995	1884	1573	1861	2000	2117	1074	2048[a]	1290	2822	2204
Predicted temperature in (°C) at a self heat rate h in (°C/min), calculated for the energetic substance alone ($\phi = 1$)											
25 (μW/g)	114.3	113.6	115.7	112.5	111.7	107.6	116.0	85.0	89.6	106.1	115.7
50 (μW/g	119.5	118.9	121.0	117.9	117.0	113.1	121.7	89.6	94.3	111.1	121.0
$h = 0.02$	140.8	140.2	142.4	139.9	138.9	135.7	145.2	108.0	113.1	131.6	142.4
$h = 0.05$	148.7	148.2	150.4	148.1	147.1	144.2	154.0	114.9	120.1	139.2	150.4
$h = 0.10$	155.0	154.5	156.7	154.6	153.5	150.8	161.0	120.3	125.6	145.2	156.7
$h = 0.50$	170.2	169.8	172.0	170.5	169.3	167.1	178.1	133.3	139.0	159.8	172.0
$h = 1.00$	177.1	176.7	178.9	177.7	176.4	174.6	185.9	139.2	145.0	166.4	178.9

25 μW/g ≡ 7.2 E-4°C/min with $C = 2.092$ J/K g.

[a] Total curve: $Q_A = 3517$ J/g, $T_{M2} = 234.6$ °C, $h_{M2} = 0.205$ °C/min, $T_{f2} = 263.5$ °C.

Table 3
Activation energies of the decomposition of some alkylazides [13,14]

Substance	Methyl-azide	Ethyl-azide	*n*-Propylazide	*iso*-Propylazide
E_a (kJ/mol)	170.7	167.8	164.9	161.1

GAP-AA-500 and octylazide have somewhat lower activation energies. In the case of octylazide to one part this may be originating from the relatively small self heat rates measured. To the other part the lower activation energy of octylazide can be caused by the stabilizing effect of the *n*-octyl group (positive induction effect) for the nitrene functionality. The activation energy of the C–N_3-group decomposition is decreasing with increasing size of the alkyl group, see Table 3.

The adiabatic heat generation rate can be determined from the adiabatic self heat rate curves. For this, the data of the specific heat capacity as a function of temperature are required of the solvent, the reactants, the decomposition products and the measuring cell. In addition the respective masses of the substances involved are needed also. So far only little is known about the decomposition products. In a first approximation, the specific heat capacity values are used as stated in Section 2.2 to calculate the ϕ-factor. This results in the formulation of the heat generation rate dQ_A/dt of a decomposing substance A according to Eq. (19).

$$\frac{dQ_A(T(t))}{dt} = \left(c_{P,s} \cdot m_S + c_{P,LM} \cdot m_{LM} + c_{P,M} \cdot m_M\right) \cdot \frac{dT_{MS}(t)}{dt} \tag{19}$$

where Q_A is the released heat from the decomposition of substance A in dimension of energy. In Table 2 the value of Q_A is given normalized to the weighed-in amount of the energetic substance. This normalization is not included in Eq. (19). $c_{P,i}$ is the specific heat capacity of substance *i*, m_i the mass of substance *i*, dT_{MS}/dt the self heat rate measured of the system 'energetic substance-solvent-measurement cell'. Index S is the energetic substance or sample, index LM the solvent, and index M the measuring cell.

Using the enthalpy of reaction $(-\Delta H_{R,A})$ for the decomposition of the substance A according to a reaction of the first order, the heat generation rate dQ_A/dt is given also by Eq. (20), where $A(T(t))$ is in mol, $M_A(T(t))$ is the actual mass of A and m_A is the molar mass of A.

$$\begin{aligned}\frac{dQ_A(T(t))}{dt} &= -\frac{dA(T(t))}{dt} \cdot (-\Delta H_{R,A}) \\ &= -\frac{dM_A(T(t))}{dt} \cdot \frac{1}{m_A} \cdot (-\Delta H_{R,A}) \\ &= (-\Delta H_{R,A}) \cdot k_1(T(t)) \cdot A(T(t_0)) \\ &\quad \cdot \exp(-k_1(T(t)) \cdot t).\end{aligned} \tag{20}$$

Figs. 13 and 14 show the dQ_A/dt curves calculated using Eq. (19) for the plasticizers GAPA and A17 (EGBAA) as examples, once as a function of temperature (used as $1/T$ with T in Kelvin on the abscissa but indicated as °C) and once as a function of the experimental self heat time. The different reaction rates can be recognized in the time representation. A17 reacts considerably slower than GAPA as the increase in temperature is slower. By integrating the heat generation rate as a function of time, one arrives at the heat Q_A generated, which is 2204 J/g for GAPA and 1861 J/g for A17. Table 2 contains all the Q_A-values and also shows the extrapolated temperatures at which a heat generation rate of 25 and 50 μW/g would be measured. Me/Et-NENA and PolyGLYN have the lowest temperature values, they are 85°C and 89.6°C for 25 μW/g. The values of the compounds with azido groups are all significantly greater than 100°C. DANPE has a relatively low value at 106.1°C, the values for the GAP samples are about 114°C. Fig. 15 shows the adiabatic self heat rate as function of the normalized self heat time. The experimental self heat time values were normalized using the respective ϕ-factor in relation to the weighed-in energetic substance. For a number of the substances investigated the adiabatic self heat rates can be seen in the time period from the times corresponding to $h = 0.05$°C/min to the times corresponding to their maxima at h_M. The scaling with the ϕ-factor gives the approximate time ranges of the decomposition reaction of the energetic substances alone.

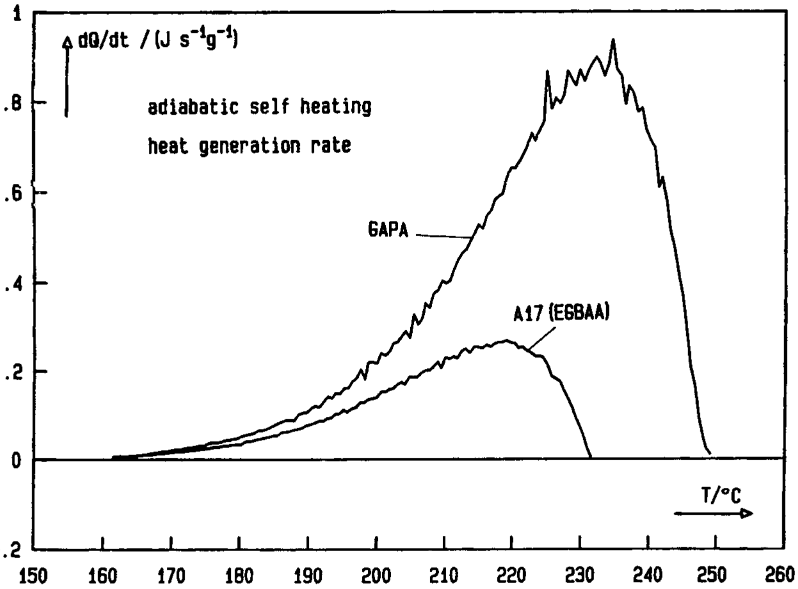

Fig. 13. Adiabatic heat generation rates of the plasticizers GAPA and EGBAA (A17) as function of the temperature reached by the self heating.

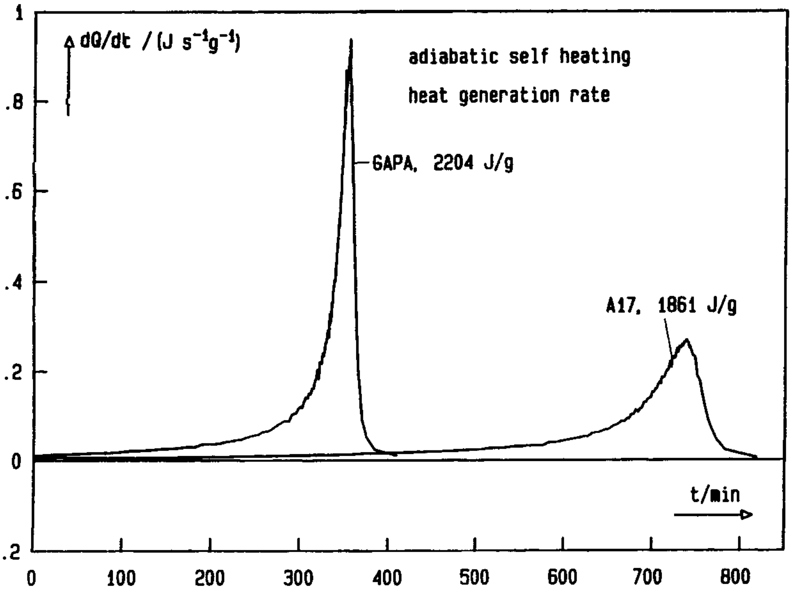

Fig. 14. Adiabatic heat generation rates of the plasticizers GAPA and EGBAA (A17) as function of the self heat time.

The presented data evaluation includes the approximations described in Section 2.2. The obtained kinetic data for the decomposition reactions agree with literature data and with the results of other measuring methods. The conclusion is the approximations made for the evaluation of the ARC^{TM} data seem

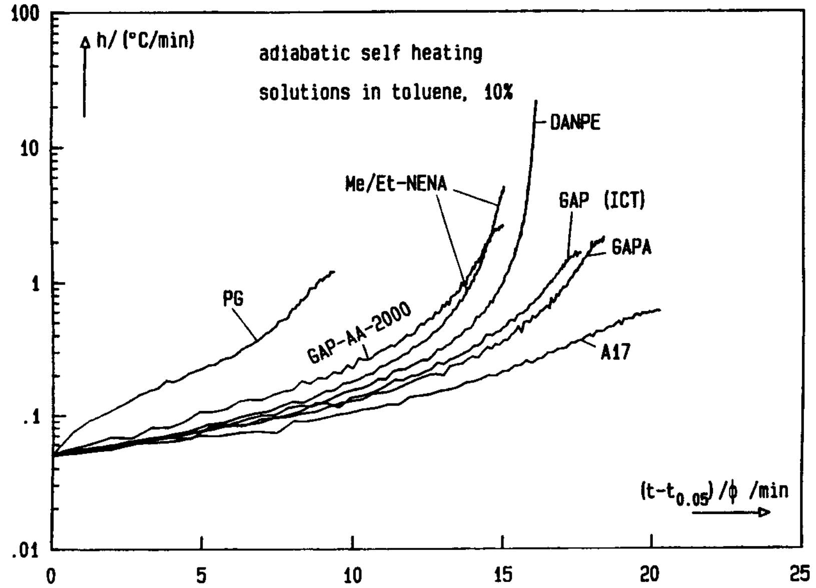

Fig. 15. Adiabatic self heat rates of some of the investigated compounds as function of the self heat time, normalized with the corresponding ϕ-factor related to the energetic substance alone. The curves are shown from $h = 0.05$°C/min on up to the maximums h_M of the $h(T)$-curves.

not to influence it. This means the adiabatic self heating can be used as a method of thermal analysis to assess the energetic substances with regard to (1) the decomposition temperature range, (2) the Arrhenius parameters obtained from the adiabatic self heat rate curves, (3) the heat generation and (4) the heat generation rate. The last two quantities contain a systematic error because of the approximations in the specific heat capacities and may be in the inert mass taken into account (further parts reduce the above given extrapolated temperatures), but they are useable for comparative purpose.

6. Summary

The adiabatic self heat rates of more recent plasticizers and non-cured binders with azido groups, nitramine groups and nitric acid ester groups were measured with an ARC™ in toluene solutions of the energetic substances with contents of about 10 mass%. The following substances were investigated: (1) mixture (58.8/41.2 in mass-%) *N*-methyl-/*N*-ethyl-NENA, (2) DANPE, 1,5-diazido-3-nitraza-pentane, (3) GAPA, short chain GAP with N_3-end groups instead of OH-end groups, (4), EGBAA (A17), ethylene glycol-bis-(α-azidoacetate), (5) octylazide, (only model substance, not intended for use in explosives), (6) GAP-AA-2000, GAP with α-azidoacetic acid esterified OH-end groups, (7) GAP-AA-500, as GAP-AA-2000, however short chains, (8) uncured PolyGLYN, poly-glycidylnitrate, (9) uncured GAP, poly-glycidylazide, one manufacturer, (10) uncured GAP, poly-glycidylazide, another manufacturer.

Using weighed-in amounts of energetic substance between 0.59 and 0.67 g a high measurement sensitivity was achieved with the ARC™. As the measurements were made in a closed measuring system, the results were not falsified by evaporation. The investigations in solutions make a controlled observation of the decomposition reactions possible. The energetic substances alone would deflagrate after a short time period of controllable self heating. The onset temperatures of decomposition were determined to be between 159°C and 174°C for compounds with azido groups. They have the values of 130°C and 146°C for Me/Et-NENA and PolyGLYN, which contain nitric acid ester groups. With the data measured one can classify the substances according to the decomposition temperature range, the energy released (heat generation Q_A) and the rate of the energy release (heat generation rate dQ_A/dt). It was possible to apply a reaction of first order to all investigated substances for the main decomposition range. A definite secondary reaction was observed only in the case of Me/Et-NENA. The activation energies are between 157 and 169.4 kJ/mol for the compounds with azido groups. Me/Et-NENA and PolyGLYN show activation energies of 165.1 and 166.8 kJ/mol respectively. The values are in the range of the bond energy of the CN–NN bond (161–170 kJ/mol) of the azido group and of the CO–NO_2 bond (160–170 kJ/mol) of the nitric acid ester group. With the examples uncured GAP alone and uncured GAP dissolved in dioxan, it was shown that the measured adiabatic self heat rate of the solution can be scaled to those of the energetic substance alone. The procedures to do this have been described.

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